High sampling standards

Paul Reagan, Sampling Associates International, US, discusses the issues to be considered when sampling petroleum coke.

Petcoke is well established as a primary carbon fuel in world energy markets and competes with coal in many applications, particularly in the cement and power generation industries. The higher grades are also used to make anodes for the aluminium industry. It is a unique commodity, however, and some important technical aspects need to be understood by both buyers and sellers. These considerations are outlined in this article, and a state-of-the-art case study in quality control is described.

Petcoke's competition with coal has become more intense in the last few years, due to a significant rise in worldwide petcoke production, which has increased by approximately 50% over the last five years. Overall tonnages have increased from approximately 40 million tpa to 60 million tpa. With even more capacity expansion planned this year, petcoke will be a major player in world energy markets.

Chemical and physical characteristics

Fuel grade petcoke is a byproduct of oil refining and is characterised by its high-carbon, low-ash, high heating value and low-volatile content. It contains commercially significant concentrations of sulphur and metals, notably nickel, vanadium and iron. The total concentration of sulphur is very high in petcoke, with a range of 2 - 6% on a dry basis. Most of the new production yields have sulphur concentrations towards the higher end of the spectrum, within the range of 4 - 6.5%. In addition to the high sulphur content, petcoke has a wide range of sizing and hardness distributions. As a result, its quality parameters are carefully scrutinised in the marketplace, and independent sampling and analysis of the material is almost always performed.

Sampling characteristics

As petcoke is a byproduct of an industrial process involving a relatively consistent raw material feed, it is often much more consistent in quality than coal, which is the result of mineral mining. As such, many people erroneously assume that the testing of petcoke is easy and straightforward. However, it is a mistake to confuse overall consistency with complete homogeneity. There is often variability within the material that must be represented in any sample that is collected.

One very important characteristic of petcoke, similar to other solid carbon fuels, particularly coal, is that the chemical and physical properties of the material are not always distributed equally between different particle sizes. Therefore, any consignment screened into its different particle sizes frequently shows that many of its commercially important properties, e.g. sulphur, volatile matter, moisture and hardness as measured by the Hardgrove grindability index (HGI), can be quite different depending upon the size fraction. As such, petcoke is not homogeneous. Tables 1 and 2 show two important parameters (sulphur and volatile on a dry basis) of three different petcoke samples, demonstrating how the contents are distributed between the different size fractions.

In Table 1, note that petcoke A has very little variation between the different size fragments. This petcoke is very easy to sample for dry sulphur content. However, petcoke B has a different variable distribution with higher sulphur exhibited in the smaller size fractions, which declines as the particle size increases.

Petcoke C is also variable, but it shows the reverse distribution, with the sulphur content rising as the size increases. If the sample is collected incorrectly in petcokes B and C, sulphur content reported by the lab will be incorrect.

Table 1. Percentage sulphur content of three petcoke samples

	0 x 6 mm	6 x 25 mm	25 x 50 mm	50 x 75 mm
Petcoke A	6.38	6.37	6.38	6.36
Petcoke B	5.16	4.76	4.85	4.56
Petcoke C	4.74	4.92	5.10	5.61

Table 2. Percentage volatile content of three petcoke samples

	0 x 6 mm	6 x 25 mm	25 x 50 mm	50 x 75 mm
Petcoke A	12.07	11.46	10.91	10.88
Petcoke B	10.52	10.44	10.00	9.64
Petcoke C	12.87	13.31	11.52	10.82

Mechanical sampling system installed on a main conveyor.

Automatic sample processing equipment.

Table 2 shows a variable distribution of dry volatile content. The general trend in all three petcokes in Table 2 is towards lower volatile in the higher size fractions. Volatile content is important because it is often associated with HGI (hardness). Although petcoke produced from different refineries has its own characteristics, a general rule that applies to most petcokes is that as the volatile content falls, the material gets harder and the HGI test result is lower.

As HGI is an important test for most petcoke consumers, a poor sample affects the HGI result. Even a fraction of 1% of volatile content can make a difference to the HGI rating. As a result of this variance in volatile content, hardness (HGI) is also unevenly distributed in particles of different sizes.

In addition to the chemical parameters discussed above, moisture content is directly related to the size distribution. Due to the increased surface area, the lower size fractions (fines) almost always contain more moisture. Therefore, an improperly collected sample will not reflect the true moisture content, which will directly affect factors such as the as-received calorific value.

This variable distribution of different parameters in different size fractions of petcoke means that proper sample collection is critical. The objective of representative sampling is to obtain the same distribution of particle size in the collected sample as in the consignment. Failure to do this means that the test results will not be representative. This is why the requirements of ASTM D 2234 (the standard for collection of a gross sample) must be followed closely.

Many quality problems associated with petcoke transactions are caused by inadequate sampling techniques. Often, the task of sample collection is assigned to plant or field personnel who do not have a sound understanding of the principles of representative sampling. Sampling is often a very small part of their overall job; they have other priorities, which can lead to short cuts that affect the integrity of the sample. They obtain some material to send to a lab as a sample, but it is not representative.

An extreme example of this is if a bag or small bucket is filled from one area of the stockpile. This can hardly be called a sample, and is more accurately labeled as a specimen. If the test results of this specimen reflect the quality of the entire stockpile, it is purely coincidental. It is important to remember that the best lab in the world cannot provide accurate results unless the sample is collected properly.

Petcoke sampling

Petcoke sampling can be carried out manually or mechanically. Manual sampling is common, but due to the sampling characteristics mentioned above it must be undertaken diligently and strictly, according to standards.

Many locations have turned to mechanical sampling to improve the quality of the sampling process. Mechanical sampling utilises machinery in order to collect a full cross section of the material required by the highest level of sampling.

There are two kinds of mechanical sampling systems, which collect a full cross section of material: cross stream (falling stream) and cross belt. The cross stream system collects the sample at the transfer point as the material falls from one conveyor to another, while the cross belt method collects it from the moving conveyor via a sweeping action.

The term 'automatic sampling' is often used when referring to sampling machines. The use of this term is incorrect, since it leads people to believe that sampling machinery does not need human attention. The correct term is mechanical sampling. Not only do the machines need to be operated correctly, but maintenance is critical to its ability to collect representative samples. In addition, they need frequent cleaning, particularly the crusher. Petcoke can be quite sticky, and cleaning the crusher can be instrumental to keeping the mechanical sampler online.

Sulphur determination equipment.

Analytical characteristics

While the process of petcoke sampling is relatively similar to coal sampling, it is important to understand that petcoke has particular analytical characteristics. One frequent problem encountered when testing petcoke is that most of the ASTM standards used routinely in analytical laboratories are standards that have been developed for coal and coke. For example, ASTM D2234 (sampling), ASTM D2013 (preparation) and ASTM D409 (grindability) are all coal standards, and do not account for the fact that petcoke is not like coal.

ASTM D-5 is the committee on coal and coke; ASTM D-2 is the committee that covers petroleum coke. However, D-2 is in fact the committee for petroleum, so petcoke is just a small part of it. As such, there are fewer specific standards for petcoke than for coal, although they are currently being formulated.

As a result, using a laboratory that has experience with petcoke and is set up to run tests for which there are petcoke standards can be important for the successful performance of analytical tests within the repeatability and reproducibility allowances. Test parameters where such experience can be helpful include HGI, sulphur and volatile matter tests. Many coal laboratories are set up to run the sulphur test, but have not had much experience of testing materials with a high sulphur range, such as petcoke.

Sampling in practice

A recent case illustrating correct sampling at work was a result of a programme set up in Mexico by Petroleos de Mexico (Pemex) and Cementos de Mexico (Cemex). Pemex has installed technology to produce petcoke in several of its refineries. Cemex has entered into a long-term contract to purchase all of the petcoke produced, which it will use in its cement plants and to provide fuel to a fluidised bed power plant, located in eastern Mexico.

The programme was designed to implement the sampling and analytical protocols to provide the following:

- Daily quality control information on production.
- An independent assessment of quality for the sales transaction.
- Rapid analyses of train and truck loadings to ensure that the final delivery point knows what it is receiving.

An additional factor was the role that the programme would play in satisfying the requirements of Pemex's ISO 9000 programme.

Mechanical sampling

The foundation of the programme starts with mechanical sampling. A cross belt-type sampler has been installed on the main loading conveyor for both rail cars and trucks.

The mechanical sampling system ensures that a full stream cross section of the petcoke on the conveyor is collected at regular intervals (the primary increment). The primary increments are reduced in top size to 4 mesh (4.76 mm), by passing it through a crusher, and then divided in mass by the secondary sampler to produce the 'final save' sample for the laboratory. Any material not taken to the laboratory is returned to the main loading conveyor via a reject conveyor.

The mechanical sampling system also has the ability to collect individual primary increments prior to crushing, in order to determine the size consist of the petroleum coke consignments.

Sampling system performance is

monitored by tracking the sampling ratio (known as the observed ratio), which is the comparison of the mass of the final laboratory sample to the mass of the material from which it is loaded. This ratio is compared to the theoretical ratios that the machine should produce (known as the design ratio) and tracked using statistical process control techniques to monitor variability and trends. Tracking of the sampling ratio provides a simple but powerful tool for assessing the performance of any mechanical sampling system.

Both the operation and maintenance of the sampling system have been contracted out to an independent third party, which assures constant attention while the equipment is operating and diligent maintenance when it is not. Maintenance is a critical task when obtaining representative samples, but often plant personnel do not perform it properly because of their competing priorities. This programme places a strong emphasis on maintenance, especially preventive maintenance.

In addition to representative samples, proper maintenance, which includes frequent cleaning, contributes to longer equipment life.

Preparation and analysis

The building that houses the crusher and secondary sampler has a segregated room for preparation and analysis. Once the mechanical sample is collected, it is immediately transported to this room for processing. The mechanical sample is divided into four equal parts, with one sample designated for Pemex, one sample for an umpire (third party analysis), one used for the chemical analysis and one used for determining the hardness (HGI). A completely separate uncrushed sample is used to determine the sizing.

As time is valuable, the programme calls for expedited analysis for those parameters that require it. As the tests all require some drying before the sample can be prepared, the preparation room is located next to the sampling system. There is plenty of room to dry the sizing samples, and the oven required for the HGI and proximate analyses is also situated here. All samples are prepared as soon as they are dry enough.

The HGI and sizing tests are carried out onsite. For proximate analyses, a laboratory has been installed near to the refinery and is available around the clock, which allows results to be available within 24 hours. This timely reporting of test results allows both parties to accomplish their objectives.

Tests that are not performed on a daily basis, such as those for vanadium, iron and nickel, are carried out periodically on a physical composite of the daily samples.

Conclusion

The most important issue in petcoke testing is the proper collection of the sample, due to the unequal distribution of chemical properties in fractions of different sizes. The sample must be collected correctly, whether by mechanical or manual means. Although the analytical tests are important, even the best lab is of no use unless the sample is collected properly.

The programme implemented by Pemex and Cemex in Mexico is a recent example of a case that incorporates all of the important elements: it collects the best sample possible, has an independent operator dedicated to the operation and care of the sampling system, requires immediate preparation of the samples, analyses them in a lab set up for petcoke, and produces the analytical data in time to make operational decisions and rapid conclusion of the sales transaction.